The Nature of Hydrogen Bonds

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Methodology

2.1 Computational details

The calculations presented in this thesis were performed by using the density functional theory-based program Amsterdam Density Functional (ADF).[1-4] We used the ADF 2016 version for the work in Chapter 3 and 4, and ADF 2017 for the work in Chapter 5. These ADF versions have been verified to give identical results. Density functional theory uses the density as central quantity, and is in principle exact. However, since the exact forms of the exchange-correlation functional $E_{XC}[\rho]$ and the corresponding potential $V_{XC}[\rho]$ are unknown, approximations of these quantities are introduced. In Chapter 3 and 5, we used the Generalized Gradient Approximation (GGA) exchange functional by Becke (B) and the GGA correlation functional developed by Lee, Yang, and Par (LYP).[5,6] In order to describe the non-local dispersion interactions, we applied the DFT-D3(BJ) method developed by Grimme, which contains the damping function proposed by Becke and Johnson and is essentially free of basis set superposition errors and other incompleteness effects.[7-9] For the work in Chapter 4 we used the GGA correlation functional developed by Perdew (P86) in combination with the B exchange functional.[10] Both the BLYP-D3(BJ) and BP86 functionals are in good agreement with the best available ab initio results for hydrogen bond lengths and energies of hydrogen-bonded systems, including Watson-Crick DNA base pairs.[11-14] All integrals that are evaluated numerically, including the exchange-correlation integrals, were solved by using Becke's integration scheme with an integration accuracy of 'very good' (Chapter 3 and 5) or 'excellent' (Chapter 4).[15]

The Kohn-Sham molecular orbitals (KS MOs) are constructed from a linear combination of Slater-type orbitals (STOs), which have the correct cusp behavior and long-range decay. We used the TZ2P basis set, which is of triple-ζ quality for all atoms and has been augmented with two sets of polarization functions, i.e. *2p* and

3d on H and *3d* and *4f* on C, N and O.[16] To speed up the computations, we treated the *1s* core shells of carbon, nitrogen and oxygen by the frozen-core approximation.[17] The molecular density was fitted by the systematically improvable Zlm fitting scheme with quality 'very good' (Chapter 3 and 5) or 'excellent' (Chapter 4).[18] The SCF procedure was considered to be converged if the difference between ρ^n and ρ^{n+1} was equal to or smaller than 1e-6.

All geometries were optimized in vacuo. The convergence criterion was 1e-5 for the nuclear gradient in Hartree/Ångström. All optimized structures with C_1 symmetry were confirmed to be true minima through vibrational analysis (no imaginary frequencies). For the hydrogen-bonded systems, planarity was enforced because this allowed us to decompose the orbital interaction into a σ and π contribution (*vide infra*). The used symmetry constraints are given in each related chapter. The molecular figures were illustrated using CYLview.[19]

2.2 Energy decomposition analysis

The bond energy ΔE is defined as the difference between the energy of the optimized complex minus the energy of the optimized monomers:

$$\Delta E = E_{\text{dimer}} - E_{\text{monomer1}} - E_{\text{monomer2}} \quad (1)$$

The energy change that is associated with the formation of the dimer is made up of two major components:

$$\Delta E = \Delta E_{\text{prep}} + \Delta E_{\text{int}} \quad (2)$$

ΔE_{prep} is the energy that is needed to deform the isolated monomers from their equilibrium structure to the geometry they acquire in the interacting system. The interaction energy ΔE_{int} corresponds to the actual energy change when the prepared (i.e. deformed) monomers are combined to form the dimer. The interaction energy can be further decomposed into a number of physically meaningful terms by using an energy decomposition analysis (EDA) approach. The EDA scheme used in this

work is based on the scheme of Morokuma[20,21] and the extended transition state (ETS) method developed by Ziegler and Rauk,[22-24] and decomposes the interaction energy into the electrostatic interaction energy ΔV_{elstat}, Pauli repulsion ΔE_{Pauli}, orbital interaction ΔE_{oi} and dispersion corrections ΔE_{disp}:[25]

$$\Delta E_{\text{int}} = \Delta V_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{oi}} + \Delta E_{\text{disp}} \tag{3}$$

The term ΔV_{elstat} is obtained by bringing the prepared monomers from infinity to the positions they have in the interacting system, resulting in an overlap between the unperturbed fragment charge distributions $\rho_A+\rho_B$. The accompanied energy change is associated with the electrostatic interaction ΔV_{elstat}, and is given by

$$\Delta V_{\text{elstat}} = \sum_{\substack{\alpha\in A \\ \beta\in B}} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} - \int \sum_{\alpha\in A} \frac{Z_\alpha \rho_B(r)}{|r\text{-}R_\alpha|}\,\mathrm{d}r - \int \sum_{\beta\in B} \frac{Z_\beta \rho_A(r)}{|r\text{-}R_\beta|}\,\mathrm{d}r + \int\int \frac{\rho_A(r_1)\rho_B(r_2)}{r_{12}}\,\mathrm{d}r_1\mathrm{d}r_2 \tag{4}$$

The first term is the repulsive Coulombic interaction between the nuclei in fragment A with those in fragment B, the second and third terms are the attractive Coulombic interactions between the electrons of monomer A with the nuclei in monomer B and *vice versa*, and the final term is the repulsive Coulombic interaction between the electrons in monomer A with those in monomer B. These terms cancel at large intermolecular separation when ρ_A and ρ_B do not overlap. However, when the fragments approach each other and ρ_A and ρ_B start to overlap, the last term actually becomes smaller than the other terms because two interpenetrating charge clouds have a smaller repulsion than point charges at the centers of charge. As a result, ΔV_{elstat} is usually attractive for neutral systems at equilibrium distance.

In the next step, the Pauli principle is obeyed by antisymmetrizing (operator $\hat{A}$) and renormalizing (factor N) the product wave function $\Psi^A\Psi^B$ that is associated with the overlapping charge densities:

$$\Psi^0 = N\hat{A}\{\Psi^A\Psi^B\} \tag{5}$$

The resulting energy change is the Pauli repulsion ΔE_{Pauli}, which comprises the destabilizing interactions between occupied orbitals and is responsible for any steric repulsion. The repulsive nature of ΔE_{Pauli} can be understood from the change in electron density when going from $\Psi^A\Psi^B$ to Ψ^0:

$$\rho^0 = \frac{1}{1-S^2}\{|\varphi_A(r_1)|^2 + |\varphi_B(r_1)|^2 - 2S\varphi_A(r_1)\varphi_B(r_1)\} \tag{6}$$

where ρ^0 is obtained by taking the modulus squared of Ψ^0.[25] Equation 6 demonstrates that antisymmetrization leads to a depletion of electron density in the overlap region and an enhancement of electron density around the nuclei. This change in electron density results in a lowering of the potential energy because of 1) a reduced electron-electron repulsion and 2) an increased electron-nucleus attraction.[26] On the other hand, the kinetic energy is going up significantly due to the greater curvature of the antisymmetrized wavefunction. Since the increase in kinetic energy is larger than the decrease in potential energy, the total energy change is actually destabilizing.

Finally, the wave function relaxes from the antisymmetrized wavefunction Ψ^0 to the final wavefunction Ψ by mixing in the virtual orbitals into the occupied orbitals. The associated orbital interaction ΔE_{oi} accounts for charge transfer (i.e. donor-acceptor interactions between occupied orbitals on one moiety with unoccupied orbitals of the other, including HOMO-LUMO interactions) and polarization (empty/occupied orbital mixing on one fragment due to the presence of another fragment). The polarization and charge transfer interactions are not further separated in this EDA scheme. The orbital interaction energy can be further decomposed into the contributions from each irreducible representation Γ of the point group of the corresponding system. For planar systems, this effectively means that we can decompose ΔE_{oi} into a σ and π contribution:

$$\Delta E_{\text{oi}} = \Delta E_\sigma + \Delta E_\pi \tag{7}$$

Finally, the term ΔE_{disp} accounts for the long-range dispersion corrections, which can be included by, *inter alia*, the atom pairwise additive DFT-D3 treatment as introduced by Grimme and co-workers.[7]

2.3 Voronoi deformation density analysis

The atomic charge distribution was analyzed by using the Voronoi deformation density (VDD) method.[27] The VDD method partitions the space into so-called Voronoi cells, which are non-overlapping regions of space that are closer to nucleus A than to any other nucleus. The charge distribution is determined by taking a fictitious promolecule as reference point, in which the electron density is simply the superposition of the atomic densities. The change in density in the Voronoi cell when going from this promolecule to the final molecular density of the interacting system is associated with the VDD atomic charge Q. Thus, the VDD atomic charge $Q_{\text{A}}^{\text{VDD}}$ of atom A is given by:

$$Q_{\text{A}}^{\text{VDD}} = -\int_{\text{Voronoi cell of A}} [\rho(r) - \rho_{\text{promolecule}}(r)]\mathrm{d}r \tag{8}$$

So, instead of computing the amount of charge contained in an atomic volume, we compute the *flow* of charge from one atom to the other upon formation of the molecule. The physical interpretation is therefore straightforward. A positive atomic charge Q_{A} corresponds to the loss of electrons, whereas a negative atomic charge Q_{A} is associated with the gain of electrons in the Voronoi cell of atom A.

The VDD scheme can be extended to the analysis of bonding between molecular fragments by computing the change in electron density that is associated with the formation of the bond. This is done by taking the sum of the prepared monomers as initial density ρ_{i}:

$$\Delta Q_{\text{A}}^{\text{VDD}} = -\int_{\substack{\text{Voronoi cell} \\ \text{of A in complex}}} [\rho_{\text{complex}}(r) - \sum_{\text{monomers}} \rho_{\text{i}}(r)]\mathrm{d}r \tag{9}$$

This method offers a direct insight into the redistribution of electronic density caused by the bond formation between the fragments. As a further analysis tool, $\Delta Q_{\mathrm{A}}^{\mathrm{VDD}}$ can be decomposed into contributions of different irreducible representations Γ of the point group of the complex. For planar molecules, this affords a distinction to be made between σ and π components. For further information on the VDD method, and a comparison between VDD and other methods for charge analysis, the reader is referred to Fonseca Guerra et al., 2004.[27]

2.4 References

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